(54) Title: COMBUSTIBILITY MONITOR AND MONITORING METHOD

(57) Abstract

An apparatus (1) for determining the concentration of a critical first component, such as hydrogen, of an atmosphere or environment (E), wherein the first component is capable of forming a combustible mixture with a second component, such as oxygen; the apparatus comprises: (A) a sampling unit (10) including: (A1) a small measuring chamber (12) operatively connected with an ignition means (135) capable of being operated so as to initiate in said chamber a combustion of said critical first component by reaction with said second component, and (A2) at least one sensor (15) operatively connected with said measuring chamber for generating a signal formed by essentially proportionate contributions from all significant components contained in said measuring chamber; (B) at least one flame arrestor (14) intervening between said measuring chamber (12) and said environment (E) of interest; and (C) a control unit (16) capable of imposing a mode of operation in at least two distinct phases wherein, during a first phase, said environment of interest is allowed to accumulate in said measuring chamber; and wherein, during a second phase, said ignition means is operated for initiating said combustion in said chamber; and (D) a means (17) for evaluating at least one signal generated by said at least one sensor before operation of said ignition means, and at least one signal generated by said at least one sensor after operation of said ignition means so as to generate a signal (S) which is indicative of said concentration of said critical first component in said environment of interest.

COMBUSTIBILITY MONITOR AND MONITORING METHOD

Field of the Invention

5   The present invention generally relates to analysis of poten-
tially hazardous mixtures of substances and specifically to
apparatus and method means for combustibility monitoring by
determining the concentration of a first critical component
in an environment or atmosphere of interest containing a sec-
10   ond component that is capable of forming a combustible mix-
ture with the critical first component. The invention is of
particular relevance for monitoring gaseous substances and
atmospheres containing them.

15   Combustible gaseous mixtures are those in which a first gase-
ous component thereof is capable of rapid exothermic reaction
with a second component of the mixture by an oxidative proc-
ess which may, but need not, involve oxygen as the oxidizing
agent. Depending upon the relative amounts of the reacting
20   components, the speed of reactions, the amount of heat gener-
ated, and the activation required for initiation of the reac-
tion, such mixtures may cause substantial hazards.

Consequently, prevention of the formation of such mixtures,
25   such as by continuous monitoring of an atmosphere of inter-
est, is of general technological importance, and may be man-
datory by law. Such monitoring is of particular importance in
substantially enclosed environments, such as housings of
processors which generate combustible or explosive gas mix-
30   tures by evolving hydrogen, possibly but not necessarily in
the presence of a surplus of oxygen, or other relatively en-
closed spaces where hazardous or potentially hazardous gas
mixtures may occur without human intervention, such as meth-
ane in the air of mines, or spaces in areas where gaseous
35   combustible chemicals or fuels are produced, processed, dis-
tributed or consumed.

The presence of elemental hydrogen in an atmosphere that con-
tains, or may come into contact with, a sufficient amount of
40   oxygen, such as air, is particularly hazardous because of the

extremely high specific amount of heat generated upon reac-
tion between hydrogen and oxygen and the extremely low acti-
vation energy required for initiation of the reaction. Thus,
hydrogen monitoring is needed in various industrial work-
5   places, e.g. in the immediate vicinities of containers delib-
erately filled with gaseous hydrogen, such as large electri-
cal transformers and nuclear or chemical reactors as well
fuel reservoirs whenever liquid or gaseous hydrogen is used
as a fuel. The atmosphere within such containers or a sur-
10   rounding enclosure will become explosive when the amount of
gaseous hydrogen as the first component attains 5 %, by vol-
ume, if oxygen as the second component is present in an at
least stoichiometrically equivalent amount or in stoichi-
ometric excess, or when at least 5%, by volume, of gaseous
15   oxygen as the first component is formed in the presence of a
stoichiometric equivalent or excess of gaseous hydrogen as
the second component.

However, while monitoring of atmospheres of interest that do
20   contain oxygen and may contain hydrogen is of particular in-
terest, the present invention is not limited to this aspect
but is applicable wherever a first component (which may be an
oxidizable or an oxidizing compound) is capable of forming a
"combustible" i.e. exothermally reactive mixture with a se-
25   cond component which provides the complement of the reaction,
i.e. is oxidizing for an oxidizable first component, or - in
reverse - is oxidizable by an oxidizing first component.
While elemental oxygen is a typical "second" component be-
cause of its universal appearance in air, other oxidizing
30   substances, notably those having a normally (i.e. under nor-
mal conditions of temperature and pressure) gaseous phase,
such as fluorine or bromine, are capable of forming exother-
mally reactive gaseous mixtures with such oxidizable gases as
hydrogen as well. Accordingly, the term "combustion" is nei-
35   ther to be understood as a limitation to reactions involving
oxygen as the oxidizing component, nor as a limitation to
monitoring of oxidizable components of mixtures.

Consequently, the term "critical first component" as used
40   herein is intended to refer generally to that particular and

potentially appearing component of an environment or atmos-
phere of interest which is monitored so as to indicate forma-
tion of a combustible mixture with a second component which
may be but need not be present in the environment of inter-
5   est.

Examples of oxidizable and typically gaseous substances of
particular interest herein other than hydrogen are low mo-
lecular hydrocarbons (methane, ethane, propane, butane, sin-
10   gly or in mixtures) as well as other organic or inorganic
substances including low boiling organic compounds, cyanogen,
carbon monoxide, hydrogen sulfide etc., which can form combu-
stible mixtures with a reactively complemental component,
such as typically oxygen, capable of fast or "explosive" re-
15   action.

The concentrations, or concentration limits, at or within
which a given pair of an oxidizable and an oxidizing compo-
nent forms an explosive mixture are known in the art of
20   chemical processing and do not require specific explanation
herein.

Prior Art

25   Various apparatus and method means for determining the con-
centration of a component of a gaseous mixture are known and
operate on various principles of detection, including meas-
urement of thermal conductivity, measurement of the heat of
combustion by calorimetry using, for example, a pellistor,
30   determination of oxidizable components of an atmosphere, and
methods based on the modification of electrical conductivity
of semiconductors caused by the electron donating properties
of oxidizable substances, cf. EP-A-0 429 397 or EP-A-0 607
756 and the literature cited therein; such prior art means
35   could, in theory, be used for monitoring of combustible at-
mospheres.

However, such prior art methods have not proved to be en-
tirely satisfactory for monitoring potentially combustible
40   atmospheres; disadvantages include inherent difficulties of

avoiding the risk of igniting the atmosphere of interest, sensitivity to interference by oxygen or other impurities, notably when electrochemical methods or the use of semiconductor are concerned, as well as insufficient stability of
5 the monitored parameters, or lack of precision and/reproducibility and, hence, poor reliability.

Prior art amperometric means for measuring elemental gaseous hydrogen are disclosed, e.g. in US-A-4 563 249. Continuous
10 monitoring of potentially hazardous hydrogen/oxygen mixtures as disclosed, for example, in US-A-4 906 339 and US-A-4 985 130 operates on the principle of selectively measuring the concentration of either component in the presence of the other and could indicate the formation of an explosive mix-
15 ture. Electrolytes are required in these methods, however, and if the electrolyte is aqueous, prolonged operation in a dry gaseous environment causes evaporation of water and requires frequent replacement of the electrolyte and precludes unattended operation for prolonged periods of time; non-
20 aqueous electrolytes, on the other hand, are not satisfactory because they cause a rapid drift of the monitoring signal.

Non-amperometric monitoring methods and apparatus such as disclosed in US-A-5 144 831 and US-A-5 255 553 (also termed
25 pulse monitoring herein) while capable of monitoring various substances that were difficult to monitor by prior art methods are operable with binary - or at least pseudo-binary- mixtures and become less reliable when the substance to be monitored is accompanied by interfering components.
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Objects and Summary of the Invention

Accordingly, a first general object of the present invention
35 are apparatus and method means for monitoring potentially explosive environments (including atmospheres within an essentially enclosed space) while avoiding or minimizing the above mentioned disadvantages of prior art, yet providing economic and completely safe apparatus and method means for continu-
40 ously analyzing or monitoring mixtures that are potentially

or actually hazardous because of their propensity for very
rapid and, sometimes, virtually spontaneous combustion, and
which suffer no interference from humidity, nor the presence
of oxygen or other impurities typical for a specific field of
5   application.

A further object of the invention are apparatus and method
means for analysis of gas mixtures by thermal conductivity
monitoring, said mixtures containing a combustible component
10   in the presence of at least one other substance which might
interfere with the chosen method of analysis, and in the
presence of non-interfering other substances, wherein meas-
urement is effected according to the pulsing method specified
in more detail below.
15

These and further objects and advantages as will become ap-
parent from the following specification are achieved, accord-
ing to a first embodiment of the present invention, by an ap-
paratus for determining the concentration of a critical first
20   component, such as hydrogen, of an environment, when the
first component is capable of forming a combustible mixture
with a second component, such as oxygen; said apparatus com-
prising:
       (A)   a sampling unit including:
25   (A1) a small measuring chamber operatively connected
             with an ignition means capable of being operated so
             as to initiate in said chamber a combustion of the
             critical first component by reaction with the second
             component, and
30   (A2) at least one sensor operatively connected with
             the measuring chamber for generating a signal formed
             by essentially proportionate contributions from all
             significant (i.e. contributing to the measurable pa-
             rameters of interest) components contained in the
35   measuring chamber;
       (B) at least one flame arrestor positioned between the
       measuring chamber and the environment or atmosphere of
       interest; and
       (C) a control unit capable of imposing a mode of opera-
40   tion in at least two distinct phases wherein, during a

first phase, the environment or atmosphere of interest is
allowed to accumulate in the measuring chamber; and
wherein, during a second phase, the ignition means is op-
erated for initiating combustion in the chamber; and

5   (D) a means for evaluating at least one signal generated
by the at least one sensor before operation of the igni-
tion means, and at least one signal generated by the at
least one sensor after operation of the ignition means so
as to generate a signal which is indicative of the con-

10   centration of the critical first component in the envi-
ronment or atmosphere of interest.

The apparatus may include means (E) for cyclically flushing
the chamber with a gas, such as air, which is free of the

15 critical first component but may contain the second compo-
nent, such as oxygen. In other words, the second component
required for explosive combustion of the first component may
be - but need not be - contained in the environment of inter-
est.

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According to a second preferred embodiment the invention pro-
vides for a method of determining the concentration of a
critical first component of an environment or atmosphere of
interest, said first component being capable of forming a

25 combustible mixture with a second component; the method ac-
cording to the invention comprises:

        (a) providing a small receiving volume in operative con-
nection with an ignition means capable of initiating com-
bustion, in the receiving volume, of a mixture containing

30   the critical first component and the second component;
        b) providing means between the receiving volume and the
environment or atmosphere of interest so as to prevent
that combustion within the receiving volume will initiate
combustion outside the receiving volume and in the envi-

35   ronment or atmosphere of interest;
        (c) permitting, during a sampling phase, a portion of the
environment or atmosphere of interest to enter into the
receiving volume;
        (d) providing at least one sensor in operative connection

40   with the receiving volume so as to generate signals

formed by essentially proportionate contributions from
all significant components contained in the receiving
volume;

(e) operating the ignition means so as to initiate com-
bustion of the mixture of the first and the second compo-
nent in the receiving volume;

(f) obtaining from the at least one sensor at least one
signal before, and at least one signal after, operating
the ignition means; and

(g) processing the signals obtained before and after op-
eration of the ignition means to generate a signal which
is indicative of the concentration of the critical first
component in the environment or atmosphere of interest.

The method according to the invention may include the addi-
tional step of flushing the receiving volume with a gas, such
as air, which is substantially free of the critical first
component, such as hydrogen.

The term "essentially proportionate contributions" with ref-
erence to the response of the at least one sensor is intended
to indicate that the contribution of each component of the
mixture in the measuring chamber should be proportionate to
the relative amounts of the components. Preferably, the con-
tributions are additive, and it is even more preferred if
such contributions are linearly additive. The preferred sen-
sors disclosed herein satisfy this requirement.
Generally, monitoring according to the invention is effected
in a prolonged if not "endless" sequence of cycles, each of
which includes at least two-phases, i.e. before and after
each operation of the ignition means, and such cycles will be
repeated as long as the monitoring process is to be contin-
ued. Cycling times can be chosen as appropriate for a given
purpose; typical cycling times may be in the range of from 1
second or less to 1 minute or more, neither limit being con-
sidered to be critical except that the response or sensitiv-
ity of the monitoring operation may suffer if cycling times
are excessive. Each cycle may, however, include one or more
additional phases as will be explained in more detail below.

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The term "in operative connection" is intended to refer either to direct connection, e.g. the ignition means or sensor is arranged within the measuring chamber, or receiving volume, or is connected therewith, e.g. by a conduit. In a simi-
5 lar manner, the measuring chamber may be positioned within the atmosphere of interest, or be connected therewith by way of one or more conduits.

The term "small" with reference to the measuring chamber of
10 the apparatus according to the invention, or with reference to the volume of the receiving space used in the inventive method, is intended to refer to a volume of the chamber or receiving space that is substantially negligible in relation to the volume of the environment or atmosphere of interest
15 outside of, or connected with, the measuring chamber or receiving space. In absolute terms, a typical measuring chamber or receiving space will have a volume of less than 1 ml, typically about 0.1 ml. so as to minimize the quantity of energy released by combustion of the mixture of reactive com-
20 ponents in the measuring chamber or receiving space.

Typically, the volume of the environment or atmosphere of interest is substantially greater, say, by more than two magnitudes than the volume of the chamber or receiving space, or,
25 in reverse, the measuring chamber or receiving volume typically will be smaller than 1 %, preferably lower than 0.1 % of the volume of the atmosphere of interest.

30 Preferred Embodiments of the Invention

The measuring chamber, or the walling which encompasses the receiving volume, preferably is made of a material that under operating conditions is essentially inert, both physically
35 and chemically, and - preferably - has a high thermal capacity such as typically stainless steel. Accordingly, stainless steel is a preferred but not limiting example of a material forming the measuring chamber or surrounding the receiving volume.

40

Generally, the parameters of the measuring chamber or receiving volume should be selected such that a temperature rise caused by combustion of the mixture of reactive components contained in the measuring chamber is reduced to negligible

5 proportions. This enhances the safety of the apparatus because it may help to avoid undesirable heating of surfaces in contact with the environment or atmosphere of interest. Further, the interpretation of a change of signal caused by combustion is simpler if there is no significant temperature

10 rise to be accounted for.

Combustion of a mixture of reactive components within the measuring chamber, or receiving volume, must not initiate combustion in the atmosphere of interest. For this purpose,

15 at least one intervening means (termed "flame arrestor" herein) is positioned between the measuring chamber, or receiving volume, and the environment or atmosphere of interest. Suitable flame arrestors in the case of gaseous components may be formed by a diffusion barrier of the type known

20 in the art, e.g. a sintered body such as a sintered plate, preferably consisting of a sintered inorganic material, e.g. a metal, such as sintered steel, or a sintered ceramic.

Alternatively, or complementally, the at least one flame ar-

25 restor may be formed by a conventional closure means, such as a valve, considered to be a "static" flame arrestor. Further, a membrane of the type specified in the above mentioned US-A- 4 906 333, US-A-4 985 130 and US-A-4 563 249 may be provided between the environment or atmosphere of interest and the re-

30 ceiving space. Such membranes are termed "semi-permeable" because they are capable of separating a normally liquid substance from a normally gaseous substance and are required if measurement is effected according to the pulsing method disclosed in US-A-5 144 831 and US-A-5 255 553, the disclosure

35 of both of which is incorporated herein by way of reference. The membrane can be incorporated into the flame arrestor or be arranged separate therefrom in a manner preventing damage by combustion within the measuring chamber or receiving space.

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Depending upon the choice of a "dynamic" flame arrestor in
the sense of permitting continuous passage of gas from the
atmosphere of interest into the measuring chamber, or receiv-
ing volume, as is the case when using a diffusion barrier, or
5   a "static" flame arrestor, such as a valve, which permits in-
terruption of the passage of the components of the environ-
ment of interest into the measuring chamber or receiving
space, sampling will be continuous or discontinuous. With
discontinuous sampling, control of the static flame arrestor
10 can be effected advantageously by the control unit which may
also control ignition time and sensor operation. Suitable
control units are available commercially or may be built from
commercially available elements.

15 A preferred type of ignition means is a heated wire or an
electrical discharge device of the type forming an arc in the
manner of spark plugs used for internal combustion engines.
Such ignition means as well as their operation is well known
in the art of combustion engines and needs no specific expla-
20 nation.

The at least one sensor can be a conventional device for
measuring the specific parameter, generally a parameter that
is capable of indicating a composition, and can be selected
25 in view of commercial availability and specific operative re-
quirements. Commercially available sensors capable of measur-
ing a thermal conductivity, or a pressure, of a combustible
mixture in the measuring chamber, are mentioned by way of ex-
ample but are not limiting. Obviously, relatively small sen-
30 sors will be preferred in view of the small volume of the
measuring chamber or of the receiving volume. More than one
sensor could be used, in or connected with, the measuring
chamber, and the same or different parameters could be meas-
ured by two or more sensors. By the same token, operation cy-
35 cles could be the same or different if more than one sensor
is used. Use of a thermal conductivity sensor is preferred
for many applications of the invention, notably when measure-
ment is made according to the pulsing method mentioned above.

Both apparatus and method according to the invention are
suitable either for measuring the concentration of an oxidi-
zable and preferably gaseous component, such as hydrogen or
low molecular hydrocarbons, as the critical first gaseous
5   component in an environment or atmosphere containing or re-
ceiving an oxidizing and preferably gaseous component, such
as elemental oxygen or air, as the second reactive component;
alternatively, both method and apparatus according to the in-
vention could be used for measuring the concentration of an
10 oxidizing component as the critical first component in an en-
vironment or atmosphere containing or receiwing an oxidizable
reactive component, such as hydrogen or a low molecular hy-
drocarbon, as the second component if monitoring of the oxi-
dizing component by conventional methods such as amperometry,
15 should present problems.

Generally, the invention is based on an interpretation of the
change of a signal generated by the at least one sensor
caused when ignition causes combustion within the measuring
20 chamber, or receiving space. This will be explained in more
detail as applied to the specific case of an atmosphere con-
taining elemental hydrogen (H_2) but similar considerations
would apply to other environments or atmospheres. Again, sen-
sors based on the measurement of thermal conductivity and of
25 pressure are used for exemplification but other detection
principles would be equally applicable in conjunction with
the invention.

30 Brief Description of the Drawings

The invention will be explained by way of illustration but
not limitation with reference to the attached drawings in
which:

35

Figure 1 is a schematic cross sectional view of a first em-
bodiment of an apparatus according to the invention;

Figure 2 is a schematic cross sectional view of a second em-
40 bodiment of an apparatus according to the invention;

Figure 3 is a diagram illustrating an example of a cycle when operating the method according to the invention;

5 Figure 4 is a diagram illustrating signal strength as a function of concentration of a critical first component when operating an embodiment of the inventive method;

Figure 5 is a diagram illustrating signal curves for differ-
10 ent concentrations of a critical first component when operating another embodiment of the inventive method;

Figure 6 is a schematic cross sectional view of a third embodiment of an apparatus according to the invention for meas-
15 uring by means of a pulsing method of operation;

Figure 7 is a diagram illustrating signal evolution when measuring by means of a pulsing method using a flushing gas; and

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Figure 8 is a diagram showing signal change when monitoring hydrogen in relation to its partial pressure in an atmosphere containing nitrogen and helium as additional components.

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Detailed Explanation of the Drawings

Figure 1 is a diagrammatic illustration of an apparatus 1 according to the invention connected via a conduit 102 with an
30 environment E, e.g. the atmosphere contained in an enclosed space (not shown) potentially or effectively containing a gas, e.g. hydrogen, that would form a combustible mixture with the oxygen that is normally present within or outside of an enclosed space which is of analytical interest because it
35 requires continuous monitoring.

Reaction chamber 12 is provided with flame arrestor in the form of a valve 14 operated by a solenoid 11 via valve stem 141. When the solenoid pushes the valve stem downwards, cham-
40 ber 12 (the reaction volume) is filled with gas entering at

the entrance port 102. Valve movement is controlled to avoid
touching the ignition means which in this embodiment is a
heating filament 135. Normally a pump and an exit port (not
shown) are provided to assist the rapid exchange of gas in
5   the reaction volume. Chamber 12 is sealed when the valve stem
is retracted. Ignition means 135 and detection means 15 are
sealed through plate 105 which closes chamber 12 and is held
in place by a collar 104. Operation of solenoid 11 is con-
trolled by a signal or signal sequence A_2 from control unit
10   16 indicated in Fig. 1 as a dash-dotted line. Also, control
unit 16 triggers ignition means 135 so that ignition is ef-
fected when valve 14 is closed. Control unit 16 is opera-
tively connected with evaluation unit 17 for proper timing of
the signals, or signal sequences before and after ignition,
15   and for producing the signal, or signal sequence S that is
indicative of the concentration of, for example, hydrogen, in
environment E.

The materials of the constituents of apparatus 1 can be cho-
20   sen to suit the application; typically, stainless steel could
be used for enclosure 101 surrounding chamber 12 and for
flame arrestor 14; sealing plate 105 preferably is made of
an insulating material, such as a ceramic, while gasket 103.
would be of a elastomeric material, such as rubber.
25

Detection means 15 then produces an initial signal character-
istic of the composition of the unreacted combustible gas
mixture. Although the choice of the type of detection means
used is not an essential part of the invention and can be se-
30   lected by those experienced in the art in view of the specif-
ics of the monitoring system required, a schematic example
given by way of illustration is depicted in Fig. 1 as a sim-
ple resistance wire 15, warmed by an electric current sup-
plied via conduits 151,152 and deposited on sealing plate
35   105.

The temperature, and hence the resistance, attained by this
wire depends upon the thermal conductivity of the gas; ac-
cordingly, the voltage developed across it by the electric
40   current could be used as a measure of the gas composition.

Heating ignition wire 135 to a high temperature (~1000 °C)
with an electric current supplied through contacts 131,132
causes the gas mixture to burn so that the combustible compo-
5   nent as well as some oxygen (or another oxidizing agent) is
removed and forms a product of the combustion reaction. The
change in the signal from detection means 15 can then be in-
terpreted to give information about the concentration of the
combustible component in the original mixture.

10

The graph illustrated in Fig. 3 presents the result of one
experiment in which a 30%H_2/Air mixture was repeatedly intro-
duced into the reaction chamber, and ignited. The ordinate
shows the signal strength S, e.g. in Volts (V) from the de-
15   tector. The abscissa indicates time (t) during a cycle from
"open valve", "close valve", and "ignite mixture" to the next
cycle beginning with "open valve". A typical cycle time in
Fig. 3 would be a period of 10 seconds.

20   The temperature changes a little as a consequence of the com-
bustion, and the signal changes during about 10 seconds fol-
lowing ignition as the system returns to the ambient tempera-
ture.

25   In practice, a calibration curve can be constructed, record-
ing the variation of signal voltage as a function of the
fraction of the combustible gas in the mixture under study.
This curve can then be consulted during analysis of an un-
known mixture to determine the concentration from the ob-
30   served signal voltage change. The diagram shown in Fig.4
presents the result of such a test. The ordinate indicates
the change of the signal S upon ignition while the abscissa
indicates the concentration of hydrogen in percent (%).

35   The embodiment of the apparatus according to the invention
illustrated in Fig. 1 above incorporates, as flame arrestor,
an isolation valve actuated by a solenoid, which can impose
limitations on the environmental conditions or working life
of the sensor. Replacement of the valve by a sintered steel
40   (or equivalent) flame barrier between environment E to be

monitored and the measuring chamber 22 as receiving volume is
illustrated in Fig. 2 and retains the advantages of the means
of entry into the volume of the atmosphere to be monitored
and of the exit of the products of the reaction out of the
5   volume, of the extinguishing of flame propagation, while also
eliminating moving parts. It should be noted that the refer-
ence numerals in Fig. 2 correspond with those of Fig. 1 ex-
cept for the first digit which corresponds with the number of
the figure. Accordingly, elements with corresponding numerals
10   in Fig. 2 are substantially the same as those in Fig.1 so
that no additional explanation is needed for Fig.2.

Apparatus 2 shown in Fig. 2 for preferred continuous opera-
tion provides for flame arresting characteristics equivalent
15   to those of a valve by means of a diffusion barrier 24 of
sufficient mechanical stability, such as a "sinter", e.g. a
body or plate made of sintered steel, which can sufficiently
impede entry of hydrogen into measuring chamber 22 for the
short duration of the combustion reaction. In quantitative
20   terms, the apparatus illustrated in Fig. 2 is characterized
by two potentially rate-determining steps: the rate of the
combustion reaction, and the rate of passage of gas molecules
from environment E into the measuring chamber 22, i.e. into
the receiving space or reaction volume, through the sinter.
25   Provided the rate of the combustion exceeds that of the per-
meation by a substantial factor, at least five or preferably
20 times, then the behavior of this simpler apparatus of Fig.
2 will emulate that of the apparatus of Fig. 1, and a simi-
lar quantitative interpretation of the results can be used.
30   Generally, the diffusion-limiting capacity of the flame arre-
stor can also be provided by a "semipermeable" membrane as
explained in more detail below.

Thus, a steady state signal can be observed at 27 for a suf-
35   ficiently long duration following ignition to permit measure-
ment results which are characteristic of the products of the
combustion. The difference between this and the signal before
ignition can then be used to calculate the fraction of the
combustible component in the atmosphere.

40

If this required inequality of the rate constants is not ob-
served, a dynamic model of the system needs to be employed to
analyze the time dependence of the signal from the detector.

5   The diagram shown in Fig. 5 represents the result of ignition
of two different mixtures of H_2 in air. Again, the strength
of the signal, e.g. in Volts, is shown on the ordinate while
the abscissa indicates time (t), e.g. spanning a period of
about 20 seconds. Point Y indicates the begin of heating the
10   ignition while point X indicates the end of heating. Curve A
is for a mixture of 15 %, by volume, of hydrogen, in air;
curve B is for a mixture of 20%, by volume, of hydrogen in
air. When only 15% of H_2 are present (curve A), the rate of
arrival of H_2 and O_2 into the burning mixture in the reaction
15   volume by permeation through the sinter is insufficient to
cause an observable change in the composition of the reaction
products. In accordance with the explanation given above, a
steady state is then observed, and the reaction products have
a constant composition characterized by a constant signal
20   from the detection means. The difference in the signals
caused by the ignition can then be interpreted to yield the
fraction of H_2 in the mixture.

When the H_2 concentration is raised to 20%, however, the ar-
25   rival rate of H_2 is sufficient to gradually change the compo-
sition of the reaction products resulting in a falling sig-
nal. This state of affairs can be countered by reducing the
permeability of the sinter.

30   Apparatus 6 shown in diagrammatic cross section in Fig. 6 re-
sembles the apparatus if Fig.2 of US-A-5 255 553 for use with
the pulsing monitoring mode except that, according to the
teachings of the present invention, an ignition means 635
connected with control unit 661 is provided and that membrane
35   643 is sandwiched between two metal screens 641,642 or simi-
lar permeable supports together forming flame arrestor 64.
Membrane 643 is permeable for the known gaseous components of
the atmosphere of interest (environment E) but is substan-
tially impermeable for liquids. Supports 641,642, on the
40   other hand, are selected for stability of arrestor 64 and

should not interfere significantly with the passage of gase-
ous components from environment E into chamber 62 because
membrane 643 acts as a diffusion control. It should be empha-
sized that the receiving volume of chamber 62 as illustrated
5   in Fig. 6 is depicted with an exaggerated volume for illus-
tration purposes only.

Apparatus 6 of Fig. 6 includes a sampling unit or probe 60
formed by a generally cylindrical casing 601, a bottom clo-
10   sure 602, and a screwed-on holding ring 604 which keeps arre-
stor 64 in a sealing connection with casing 601. Measuring
chamber 62 includes a sensor 65, typically a thermoconductiv-
ity sensor, and an ignition means 635, typically in the form
of a platinum wire which can be heated to an ignition tem-
15   perature by means of an electrical supply 671 which, together
with connecting line 672 of sensor 65, is passed through a
tubular guide 67 to plate 69 which may include a printed wire
board for signal processing.

20   Chamber closure 606 is held by a screwed-in insert 605 and a
sealing ring 607 in sealed connection with casing 601. Con-
duits 661,662 are provided for passing a flushing gas, typi-
cally air, from a source of pressure or suction (neither
shown in Fig.6) into chamber 62. Conduit 661 is shown to com-
25   prise a valve 68 with an electrical actuator line 673 for
controlling flushing of chamber 62. However, control valve 68
might be arranged in conduit 662, or each conduit could be
provided with a control valve of its own.

30   Control of operation including timing of flushing, accumula-
tion, ignition and any other phases of operation can be com-
bined with signal processing and signal evaluation by comput-
ing means in an integral unit 61 to generate signal S. Alter-
natively, operation control and signal processing can be ef-
35   fected in separate control and computation means.

A preferred method of cyclically operating an analyzer of the
type shown in Fig. 6 is as follows:

18

(i) in a first phase of each cycle, chamber 62 is purged with air via conduits 661,662 and thermal conductivity of this air charge is measured to give a first signal or signal sequence;

(ii) after closing control valve 68, accumulation of combus-
5   tible and interfering gases from environment E passing by diffusion through membrane 643 into chamber 62 is permitted during a second phase of each cycle to produce a second sig- nal or signal sequence at or near the end of the accumulation period;

10   (iii) a third phase of each cycle starts with igniting the gases contained in chamber 62 by actuating ignition 635 to generate a third signal or signal sequence which is charac- teristic of the products of the combustion reaction.

15   By means of the computations explained in mathematical term below, signal (S) is computed from:

- an interpretation or evaluation of the difference be- tween the signals or signal sequences emitted by ther- mal conductivity sensor 65 during the second and third
20   phase to produce a measure of the partial pressure of the combustible gas, and

- an interpretation or evaluation of the difference be- tween the signals or signal sequences emitted by ther- mal conductivity sensor 65 during the first and second
25   said phases to produce a measure of the partial pres- sure of the interfering gas.

Optionally, each measuring cycle may include an additional or fourth intermediate phase for permitting dissipation of heat
30   generated by ignition and computing a correction for use in computing signal S.

The following examples are given to illustrate operation of the inventive method including mathematical treatment of the
35   parameters of measurement.

EXAMPLE 1

The apparatus used was essentially as explained in Fig. 1.
40   Sensor 15 was a conventional monolithic miniature solid-state

thermal conductivity detector (Hartmann & Braun, Germany) for measuring thermal conductivity of a gas mixture.

The atmosphere of interest consisted of H_2, O_2, N_2, water vapor, and impurities, enclosed in a small volume V. The thermal conductivity is represented by λ which may be expressed, to a good approximation, as a linear combination of terms containing products of the mole fractions x_j and the thermal conductivities λ_j of each of the components:

$$\lambda = x_H \lambda_H + x_O \lambda_O + x_N \lambda_N + x_W \lambda_W + x_I \lambda_I$$

Now, the mixture is ignited so that all of the H_2 burns in the excess of O_2:

$$2H_2 + O_2 = 2H_2O$$
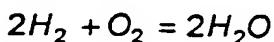
and the thermal conductivity is measured again:

$$\lambda^1 = x_O^1 \lambda_O^1 + x_N^1 \lambda_N^1 + x_W^1 \lambda_W^1 + x_I^1 \lambda_I^1$$

It will be appreciated that the thermal conductivities of the components $(\lambda_H^1$ etc.) may have changed from their values before the ignition $(\lambda_H$ etc.) because of a temperature change.

The relations between the mole fractions before and after the ignition can be expressed as follows:

$$x_N^1 = x_N / (1 - x_H / 2)$$

$$x_I^1 = x_I / (1 - x_H / 2)$$

$$x_O^1 = \frac{o \quad H}{1 - x_H / 2}$$

$$x_W^1 = \frac{w \quad H}{1 - x_H / 2}$$

Accordingly, one may write:

$$\lambda^1 = [1 / (1 - x_H / 2)] * (x_O \lambda_O^1 + x_N \lambda_N^1 + x_W \lambda_W^1 + x_I \lambda_I^1) + [x_H / (1 - x_H / 2)] * (\lambda_W^1 - \lambda_O^1 / 2)$$

Assuming there is a delay to allow the heat released by the ignition to dissipate so that the temperatures and the thermal conductivities of the components return to the values they had before the ignition $(\lambda_H^1 = \lambda_H$ etc.), the thermal conductivity of the mixture resulting from the ignition can be expressed by:

$$\lambda^1 = [1/(1 - x_H/2)] * (\lambda - x_H * \lambda_H) + [x_H/(1 - x_H/2)] * (\lambda_W - \lambda_O/2)$$

or

$$\lambda^1 * (1 - x_H/2) = \lambda + x_H * [\lambda_W - \lambda_H - \lambda_O/2]$$

This form of the mathematical expression is particularly con-

5 venient because it contains only one composition dependent term, x_H, which can therefore be isolated explicitly:

$$x_H = \frac{\lambda^1 - \lambda}{\lambda^1/2 + \lambda_W - \lambda_H - \lambda_O/2} = \frac{\lambda^1 - \lambda}{\lambda^1/2 - a}$$

where

10 $a = \lambda_H + \lambda_O/2 - \lambda_W$

Provided that a (or λ_O, λ_W, and λ_H) is known, and λ and λ^1 are measured, the mole fraction of H_2 in the atmosphere can be calculated. The value of a can be found by a calibration
15 procedure using an atmosphere of known composition.

EXAMPLE 2

Another embodiment of the method according to the invention
20 is carried out by measuring pressures and temperatures before (P, T) and after (P^1, T^1) ignition. Assuming that the atmosphere of interest behaves substantially as an ideal gas, the ratio of the total number of moles of gas before ignition to that after ignition is

25

$$\frac{1}{1 - x_H/2} = \frac{PV/T}{P^1V^1/T^1}$$

From this expression the parameter X_H can be recovered to give an explicit relation for the mole fraction of H_2. Temperature variations due to ignition are accounted for in this
30 equation, but again, the interpretation is simplified if the temperature and volume variations are negligible.

This mathematical analysis is appropriate for a steady state system in which the quantity of gas enclosed in the receiving volume is constant as is the case with an apparatus according
35 to Fig.1. When using an apparatus of the type illustrated in Fig. 2 where the flame arrestor 24 is a sintered steel plate, continuous diffusion of the atmosphere to be monitored into the receiving volume occurs during the ignition period, so

feeding more fuel to the burning mixture. It is unlikely that all components of the mixture would diffuse equally rapidly through the sinter, so that the gas composition emerging into the receiving volume could have a different composition from

5   that in the original atmosphere. This would cause the signal from the detector to vary in time (a dynamic technique) following the ignition, but in principle, the shape of the signal versus time envelope still contains information about the composition of the atmosphere to be monitored.

10

EXAMPLE 3
Analysis of the waste gases issuing from a nuclear reactors

As is well known in the art of operating nuclear reactors, it

15 is essential that, prior to releasing the gases from within the reactor into the environment, hydrogen is removed by a recombination device or "recombiner" by catalytic reaction with a stoichiometrically equivalent amount of oxygen.

20 In prior art practice, the presence of helium interferes with the determination of the quantity of elemental hydrogen in the gas mixture by standard analyzers based upon measuring thermal conductivity. However, application of the embodiment of the invention according to this example allows determina-

25 tion of the partial pressure of elemental hydrogen from the rate of change of thermal conductivity during the combustion period, when the hydrogen burns to water, and if desired, the partial pressure of helium from the combination of this result with the rate of change of thermal conductivity signal

30 during the accumulation phase.

To this end an apparatus of the type shown in Fig. 6 was used in combination with the pulsing method disclosed in US-A-5 144 831 and US-A-5 255 553 with particular reference to Fig-

35 ures 7 and 8 of the present drawings.

The atmosphere issuing from standard nuclear reactors (as environment E of this example) is known to consist of hydrogen, helium and nitrogen. The thermal conductivity of nitrogen is

40 sufficiently close to that of the purge gas (air) so that ni-

22

trogen is not an interfering component. Helium, on the other
hand, has a thermal conductivity substantially different from
that of the purge gas as well as from that of hydrogen and,
thus, interferes with determination of the partial pressure

5   of hydrogen which, in turn, has a thermal conductivity sub-
stantially different from that of air (purge gas) and nitro-
gen.

In other words, the expressions "interference" or "interfer-

10   ing component" used in the context of the present invention
are relative terms; in fact, this embodiment of the inventive
method can be used for determination of the partial pressure
of hydrogen, and/or or for determination of the partial pres-
sure of helium in a gas mixture containing these two compo-

15   nents plus any further component(s) which - as in the case of
nitrogen - has or have a thermal conductivity close to that
of the purge gas (air) and presents no interference..

In this mode of operation, thermal conductivity detector 65

20   produces a signal or signal sequence characteristic of the
composition of the gas mixture contained in reaction chamber
62, isolated from the sample or environment E to be measured
by flame arrestor 64 including membrane 643. Measurements are
taken periodically in a virtually endless series of identical

25   cycles controlled by a microprocessor arranged, for example
within control unit 61, each cycle comprising a purging
phase, an accumulation phase and a combustion phase.

Fig. 7 illustrates signal evolution during each cycle of

30   measurement; time t is shown on the abscissa. The strength of
signal S is shown on the ordinate, e.g. in terms of voltage,
starting at V_0 and dropping, during a first period t_1 to V_1
which is the signal strength at the moment of ignition M_1. As
a consequence of ignition, the signal rises to a value V_2. As

35   indicated by dotted line E_h the actual signal obtained upon
ignition is increased by the effect of heat generated when
operating filament 635 to initiated combustion; this heat is
dissipated, however, at the end of the second accumulation
period t_2 when signal strength has dropped to V_3.

40

During the purging phase of each cycle, electrically con-
trolled valve 68 is opened to allow air to flush chamber 62
via conduits 661,662 in order to obtain a background signal
from thermal conductivity detector 635 characteristic of pure
5　air. Purging with air also provides an excess of oxygen for
burning hydrogen as the combustible component during the sub-
sequent combustion phase.

At the start of period t_1, electrically controlled valve 68
10　is closed and gases diffuse through membrane 643 from the me-
dium or environment E to be analyzed into chamber 62 mixing
with the air remaining from the purge. The rate of change, or
slope, of the thermal conductivity signal S is as follows:

$$S = k_1P_1 + k_2P_2$$

15　in which k_1 and k_2 are constants while P_1 and P_2 are the par-
tial pressures of the combustible gas (hydrogen) and of the
interfering gas (helium).

Magnitude and temperature dependence of constant k_1 can be
20　determined by analyzing the rate of change of the signal
throughout the temperature range of interest, due to a known
constant pressure of the combustible gas in the absence of
the interfering gas ($P_2 = 0$); k_2 results from a similar pro-
cedure in the absence of the combustible gas ($P_1 = 0$).
25

Platinum filament 635 is heated to initiate combustion of the
gas mixture which has accumulated in chamber 62 by diffusion
from environment E through membrane 643. Combustion is pre-
vented from spreading into environment E to be monitored by
30　flame arrestor 64 including membrane 643 sandwiched between
and supported by its metallic supports in the form of screens
or sinter plates 641,642. When operating according to the in-
ventive method, the change of the thermal conductivity signal
δV as a result of the combustion will be linear and uniquely
35　correlated with the partial pressure of the combustible com-
ponent in environment E which is to be monitored:

$$\delta V = a + b*P_1$$

thus providing for measurement of P_1 from the rate of change
of δV. This is due to the fact that the change of the gas
40　composition within chamber 62 caused by removal of some oxy-

gen by reaction with the combustible component - hydrogen -
and formation of combustion product (water) may be expressed
directly in terms of the original partial pressure of the
first component.

A factor to be considered when measuring δV is the effect of
the heat generated by filament 635 on the thermal conductiv-
ity signal. This can be compensated by measuring the signal
at the end of a further accumulation period chosen to be long
enough to permit this spurious heat to dissipate. Assuming
that the rate of change of the signal during this period is
the same as during the first accumulation period, were it not
for the heating effect, quantity δV can then be calculated.

A calibration curve is established by measuring the magnitude
of this change in gas mixtures of known composition so that
constants a and b can be determined. Again, a temperature de-
pendence of parameters a and b can be quantified by analyzing
the temperature range of interest.

The calibration curve obtained is used to calculate the par-
tial pressure of the combustible component in the atmosphere
E of interest when measuring its content of the first compo-
nent. This result is combined with the rate of change of the
thermal conductivity signal during the accumulation period
and the partial pressure of interfering gas may also be cal-
culated.

In the practice of this embodiment of the invention, the rate
of change of signal during the first accumulation period is
linear in time while the rate of change of signal S is as
follows:
$$S = (V_0 - V_1)/t_1 = -(k_1 * P_1 + k_2 * P_2)$$

The signal after combustion V_2 (and therefore the signal jump
δV) can be calculated as follows:
$$\delta V = V_2 - V_1 = V_3 + S * t_2 - V_1 = a + b\, P_1$$
Hence:
$$P_1 = \{V_3 - V_1 + t_2 * (V_0 - V_1)/t_1\}/b - a$$
and

$$P_2 = -\{(V_0 - V_1)/t_1 + k_1 * P_1\}/k_2$$

Temperature should also be measured for correction or nor-
malization and appropriate values are calculated for con-
5   stants k1, k2, a, and b at the actual temperature of opera-
tion.

To demonstrate the validity of this approach, a series of gas
mixtures of known composition (at a constant temperature of
10   30°C and a pressure 970 mbar) was prepared containing from
Zero to 90% by volume of H_2, 10% by volume of He, and from
Zero to 90% by volume of N_2. These mixtures were analyzed as
described and the results are illustrated in Fig. 8 which
shows the dependence of the signals obtained upon the per-
15   centage of H2 in the gas mixtures. The straight line of least
squares through the measuring points obtained by the experi-
ment is expressed by the following equation:

$$\text{Signal} = \delta V = a + bP_1$$

where a = 4.022 mV and b = 410.8 mV/bar. In this manner, the·
20   partial pressures of H_2 and He within the nuclear reactor
were measured and monitored according to the invention.

Generally, the inventive apparatus and method are capable of
analyzing hazardous or potentially hazardous atmospheres with
25   adequate accuracy within the range of concentrations of in-
terest. The interpretation based on the change of properties
of the atmosphere caused by the ignition (a differential
technique), rather than on absolute measurements, is capable
of producing results independent of interference by other
30   components. The interposition of at least one flame arrestor
between the atmosphere of interest and the measuring chamber
excludes the risk of ignition of the gas mixture by heated or
catalytically active surfaces. The incorporation of two or
more independent, e.g. distanced, flame arrestors rather than
35   only one can be desirable if safety of operation is to be in-
creased.

It should be noted that the specific type of parameter of the
gas mixture in the measuring chamber or in the receiving vol-
40   ume is not believed to be overly critical and the examples

given above are preferred for many uses because of their lin-
ear additive contributions of the components in the atmos-
phere of interest but are by no means understood as a limita-
tion. In other words, one and the same property should be
5   measured before and after ignition of the mixture of compo-
nents such that the combustion reaction has proceeded to com-
pletion and thermal conductivity is the preferred property
for many applications of the invention.

10   It will be apparent from the above disclosure that the inven-
tion provides for inexpensive, interference-free method of
determining the partial pressure of a combustible component
in a gas mixture containing two or more components, suitable
for continuous, unattended, in-line monitoring.Various modi-
15   fications of the above will be apparent to those experienced
in the art. The scope of the invention is to be construed
from the following claims.

27

<u>Claims</u>

1. An apparatus (1;2;6) for determining the concentration of
a critical first component of an environment (E), said first
5 component being capable of forming a combustible mixture with
a second component; said apparatus comprising:
(A) a sampling unit (10;20;60) including:
    (A1) a small measuring chamber (12;22;62) operatively
    connected with an ignition means (135;235;635) capable of
10 being operated so as to initiate in said chamber a com-
    bustion of said critical first component by reaction with
    said second component, and
    (A2) at least one sensor (15;25;65) operatively connected
    with said measuring chamber for generating a signal
15 formed by essentially proportionate contributions from
    all components contained in said measuring chamber;
(B) at least one flame arrestor (14;24;64) intervening be-
tween said measuring chamber (12;22;62) and said environment
(E) of interest; and
20 (C) a control unit (16;26;661) capable of imposing a mode of
operation in at least two distinct phases wherein, during a
first phase, said environment of interest is allowed to accu-
mulate in said measuring chamber; and wherein, during a sec-
ond phase, said ignition means is operated for initiating
25 said combustion in said chamber; and
(D) a means(17;27;662) for evaluating at least one signal
generated by said at least one sensor before operation of
said ignition means, and at least one signal generated by
said at least one sensor after operation of said ignition
30 means so as to generate a signal (S) which is indicative of
said concentration of said critical first component in said
environment of interest.

2. The apparatus (1;2;6) of claim 1 wherein said first and
35 said second component are gaseous, said first component pref-
erably being hydrogen and said second component preferably
being oxygen.

3. The apparatus (2;6) of claim 1 or 2, wherein said at least
40 one flame arrestor (24;64) comprises a diffusion barrier ar-

●   ●

ranged between said environment (E) and said measuring cham-
ber (22;62).

4. The apparatus (6) of any of claims 1 - 3 comprising a
5 semi-permeable membrane (643) arranged between said environ-
ment (E) and said measuring chamber (6).

5. The apparatus (1;2;6) of any of claims 1 - 4 wherein said
at least one sensor (15;25;65) is capable of measuring a
10 thermal conductivity or a pressure of a gaseous mixture in
said measuring chamber.

6. The apparatus (1;2;) of any of claims 1 to 5 wherein said
control unit (16;26) includes a first actuating control for
15 said ignition means and, if said arrestor is a closure means,
a second actuating control for said closure means.

7. The apparatus (6) of any of claims 1 - 6 comprising means
(661;662) for passing a flushing gas containing said second
20 component through said chamber (62) and means (68;673) for
controlling such passage.

8. A method of determining the concentration of a critical
first component of an environment (E) capable of forming an
25 explosive mixture with a second component; said method com-
prising:(a) providing a small receiving volume (12;22;62) in
operative connection with an ignition means (135;235;635) ca-
pable of initiating combustion in said receiving volume of a
mixture containing said critical first component and said
30 second component;
(b) providing flame arrestor means (14;24;64) between said
receiving volume and said atmosphere of interest;
(c) permitting, during a sampling phase, a portion of said
environment of interest to enter into said receiving volume
35 in a continuous or discontinuous manner;
(d) providing at least one sensor (15;25;65) in operative
connection with said receiving volume so as to generate sig-
nals formed by essentially proportionate contributions from
all components contained in said receiving volume;

(e) operating said ignition means so as initiate combustion of said mixture in said receiving volume;

(f) obtaining from said at least one sensor at least one signal before, and at least one signal after, operating said ig-
5 nition means; and

(g) processing said signals obtained before and after operation of said ignition means to generate a signal (S) which is indicative of said concentration of said critical first component in said environment of interest.
10

9. The method of claim 8 wherein said first component is hydrogen while ~~and~~ said second component is oxygen.

10. The method of claim 8 or 9 wherein a flushing gas con-
15 taining said second component is passed through said chamber (62) prior to said sampling phase.

11. The method of any of claims 8 - 10 characterized by imposing a mode of operation in at least three distinct phases
20 wherein, during a first phase, said chamber (62) is flushed with a gas containing said second component; during a second phase said environment is allowed to accumulate in said chamber; and during a third phase said ignition means (635) is operated.
25

12. The method of claim 11 wherein said mode of operation includes a fourth phase for temperature equilibration after ignition.

30 13. The method of any of claims 8 - 12 wherein said sensor is capable of measuring a thermal conductivity.

14. The method of any of claims 8 - 13 wherein each operation
35 of said ignition is coordinated with said obtaining of said signals to constitute a cycle comprising one operation of said ignition, at least one signal before ignition, and at least one signal after ignition; and wherein said method comprises performing a sequence of such cycles.
40

15. The method of claim 14 wherein each cycle includes a phase of flushing said receiving volume with a gas which is free of said first component.

5   16. The method of claim 15 wherein said flushing gas contains said second component.

17. The method of any of claims 8 - 16 for measuring the concentration of an oxidizable gas, such as hydrogen or a low
10   molecular hydrocarbon, as said critical first gaseous component by combustion in the presence of an oxidizing gas, such as elemental oxygen, as said second gaseous component in an amount sufficient, at least for stoichiometric reaction with said critical first component.

15

18. The method of claim 8 wherein said sampling unit comprises a membrane permeable for gases and arranged between said chamber (62) and said atmosphere or environment to be monitored, said chamber including: a means (661,662) of purg-
20   ing the said chamber with air, a thermal conductivity sensor (65) which produces a signal (S) characteristic of the composition of the gas mixture contained within said chamber at any moment, and at least one means (635) of ignition of the gases contained within the chamber,
25   said method including at least three phases of operation under the control of an electronic control unit (661), wherein:
(i) a first phase for purging said chamber with air and permitting measurement of thermal conductivity of said air to give a first signal;
30   (ii) a second phase for permitting accumulation of combustible and interfering gases from said environment in said chamber by diffusion through said membrane and producing a second signal at the end of the accumulation period; and
(iii) a third phase for igniting the gases contained in said
35   chamber at the end of said accumulation period and generating a third signal which is characteristic of the reaction products,
said signal (S) being computed essentially from
   - an evaluation of the difference between the signals
40   emitted by said thermal conductivity sensor during said

second and third phase to produce a measure of the par-
tial pressure of the combustible gas, and
- an evaluation of the difference between the signals
  emitted by said thermal conductivity sensor during the
  first and second said phases to produce a measure of
  the partial pressure of the interfering gas.

19. The method of claim 18 comprising a fourth phase for per-
mitting dissipation of heat generated by said ignition, and
computing a correction for use in computing said signal (S).

I/4

11

1

E

141

14

102

101

12

135

10

103

104

16

131

105

151 152

132

S ← 17

Fig. 1

2

235 E 24

201

22

203

20

204

25

231

251 252

232

S ← 26 27
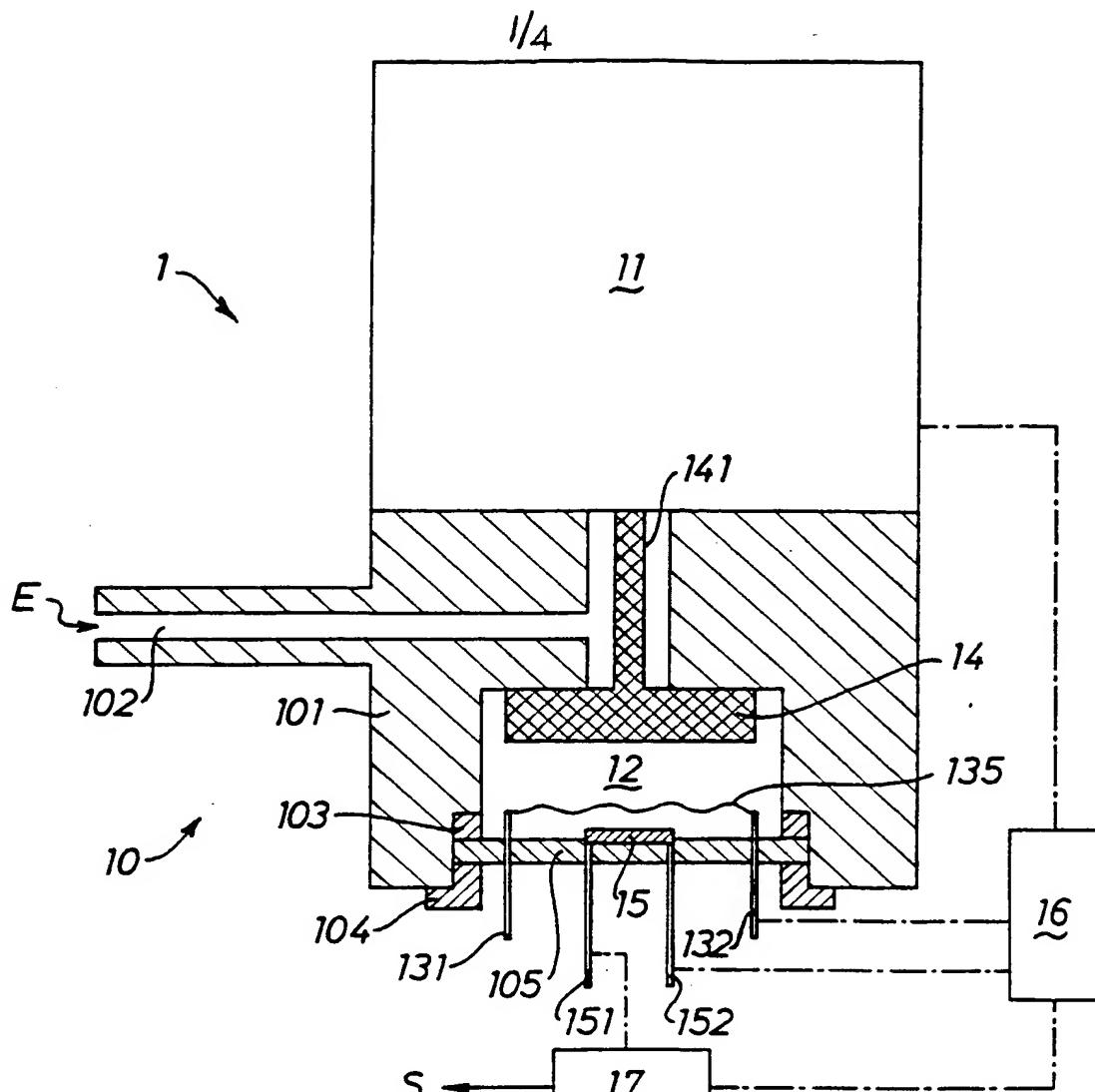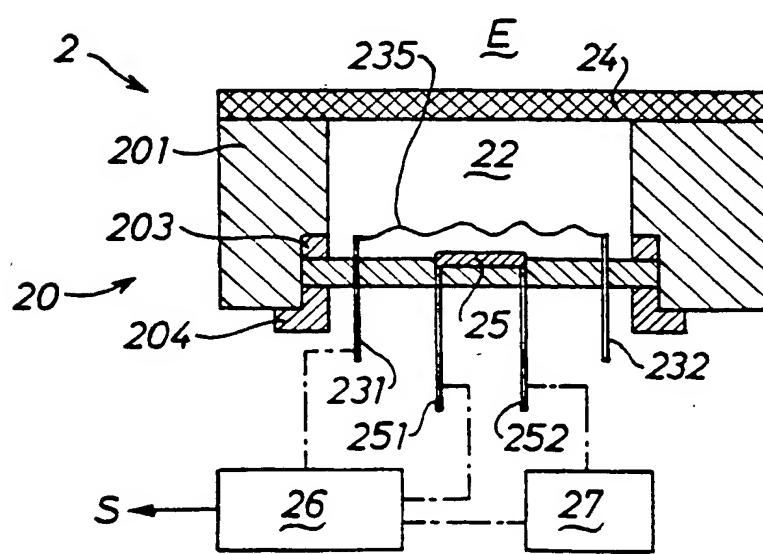
Fig. 2
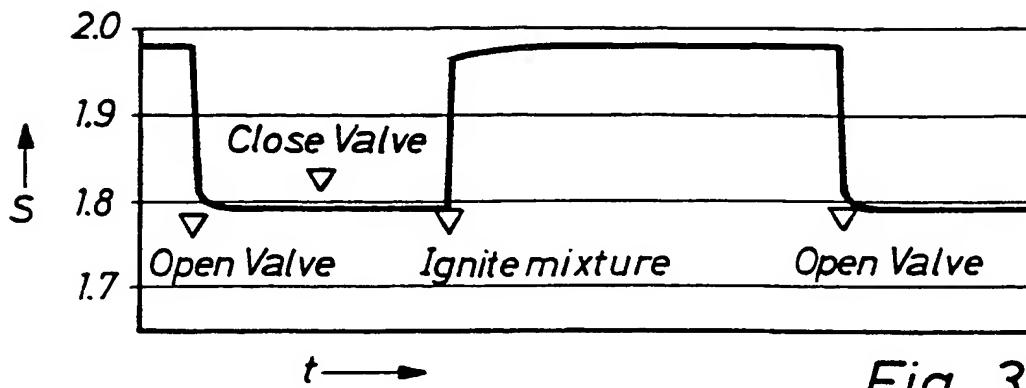
Fig. 3
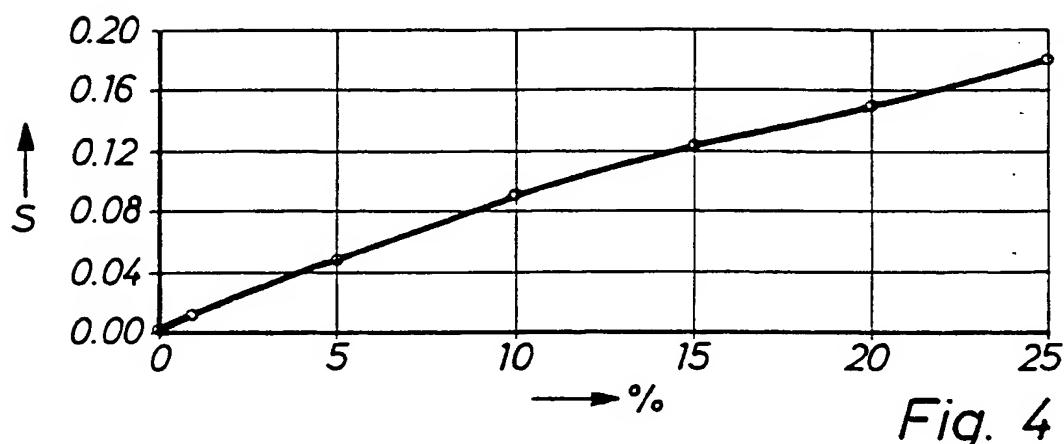
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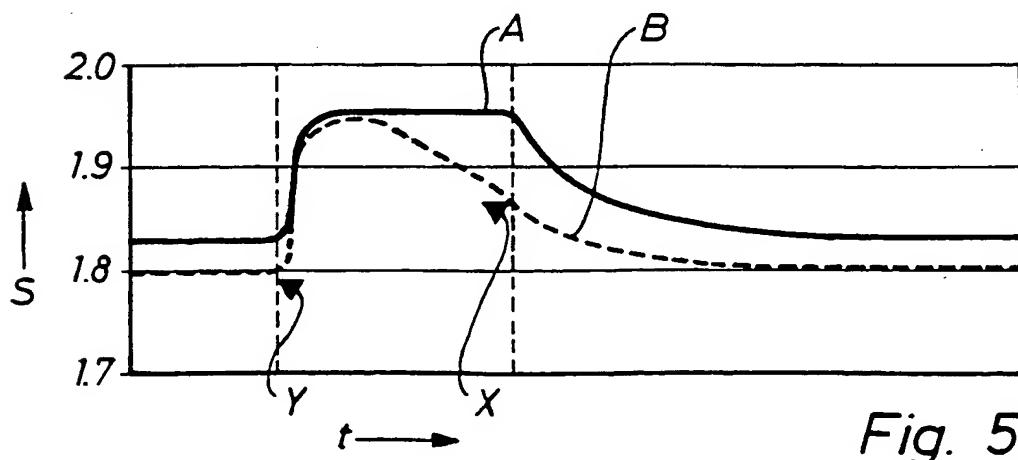
Fig. 5
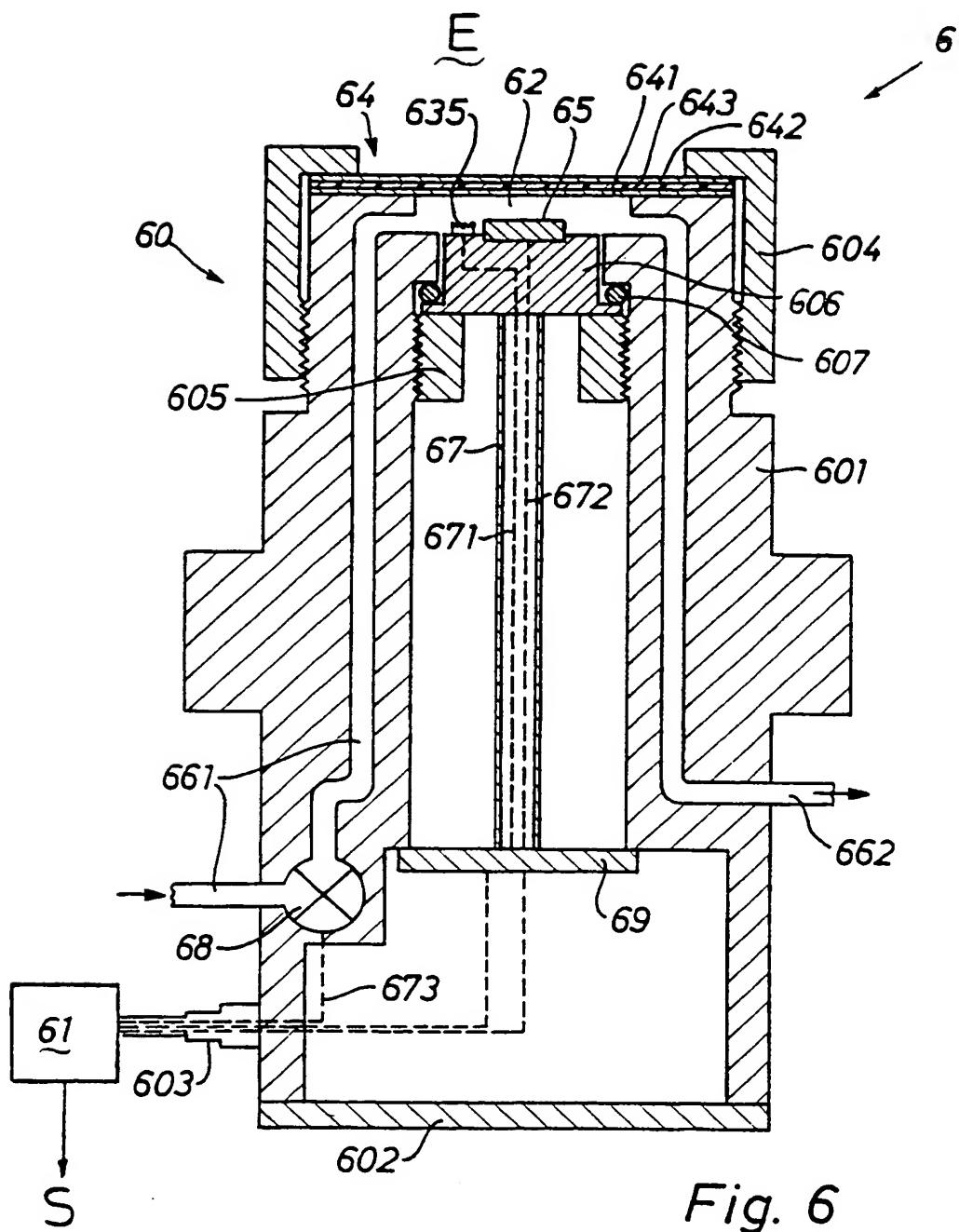
Fig. 6
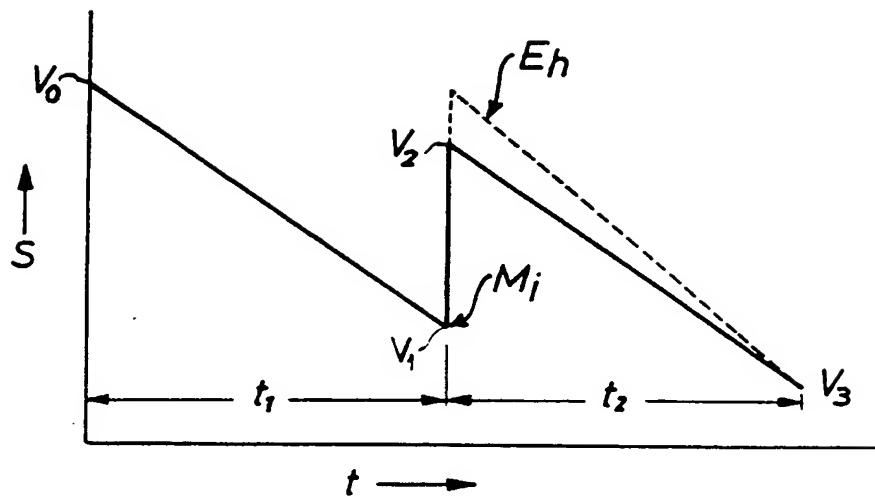
Fig. 7
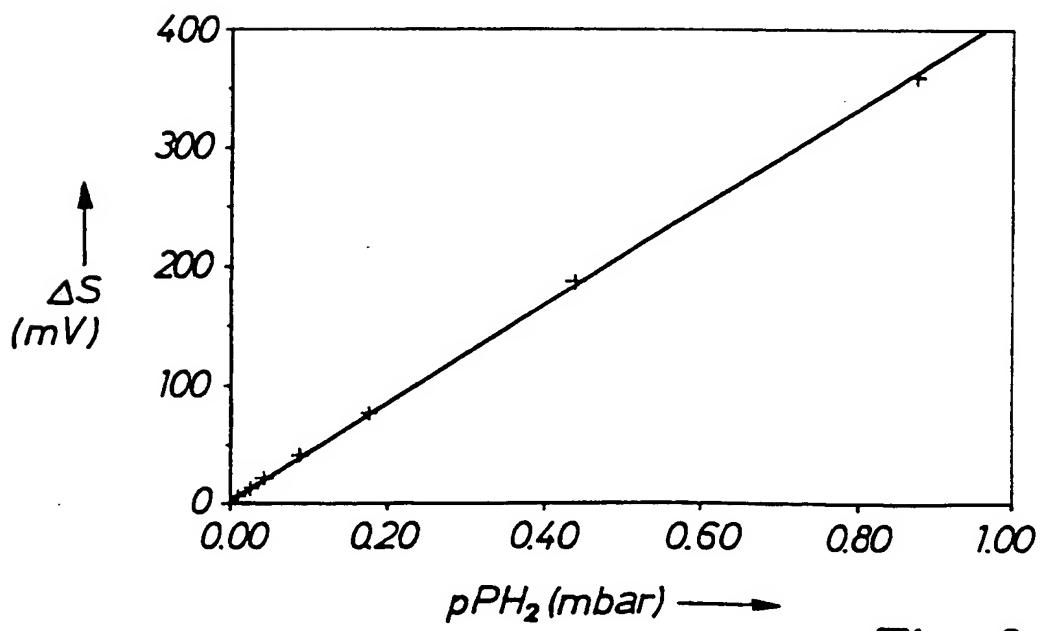
Fig. 8

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